

Oxidation of Carbon Based First Wall Materials of ITER

R.Moormann 1), H.-K.Hinssen 1), C.H.Wu 2)

1) Forschungszentrum Jülich/ISR, D-52425 Jülich, Germany

2) EFDA/Max-Planck Institut für Plasmaphysik, D-85748 Garching, Germany

email contact of main author: r.moormann@fz-juelich.de

Abstract: The safety relevance of oxidation reactions on carbon materials in fusion reactors is discussed. Because tritium codeposited in ITER will probably exceed tolerable limits, countermeasures have to be developed: In this paper ozone is tested as oxidising agent for removal of codeposited layers on thick a-C:D-flakes from TEXTOR. In preceding experiments the advantageous features of using ozonised air instead of ozonised oxygen, reported in literature for reactions with graphite, is not found for nuclear grade graphite. At 185 °C = 458 K ozone (0.8 - 3.4 vol-% in oxygen) is able to gasify the carbon content of these flakes with initial rates, comparable to initial rates in oxygen (21 kPa) for the same material at > 200 K higher temperatures. The layer reduction rate in ozone drops with increasing burn-off rapidly from about 0.9 - 2.0 µm/h to 0.20 - 0.25 µm/h, but in oxygen it drops to zero for all temperatures ≤ 450°C = 723 K, before carbon is completely gasified. Altogether, ozone seems to be a promising oxidising agent for removal of codeposited layers, but further studies are necessary with respect to rate dependence on temperature and ozone concentration even on other kinds of codeposited layers. Furtheron, the optimum reaction temperature considering the limited thermal stability of ozone has to be found out and studies on the general reaction mechanism have to be done. Besides these examinations on codeposited layers, a short overview on the status of our oxidation studies on different types of fusion relevant C-based materials is given; open problems in this field are outlined.

1. Introduction

Oxidation of codeposited layers of carbon with tritium, formed on cooler parts of the vacuum vessel (≤ 400 °C = 673 K), is a safety relevant process due to the high amount of tritium being released, and oxidation kinetics under accidental conditions (air ingress by loss of vacuum accident, steam ingress by loss of cooling into vacuum) has to be studied for these layers: If codeposited layers, which are mainly amorphous but with a high content of sp³ (diamond like) bondings ('hard' a-C:H-layers), are growing to a thickness > 25 µm they tend to break away from the substrate, forming loose flakes, which may accumulate in the vessel bottom; these flakes can easily be lifted off in loss of vacuum events, a fact, which increases their potentially hazardous features. Because such codeposited layers are a severe problem during maintenance and repair work too, there is an urgent need for a method of controlled removing of these layers; one method in discussion is application of oxidising gases at intermediate temperatures (preferably ≤ 250 °C = 523 K): Oxidation at higher temperatures causes problems because these temperatures cannot be achieved at the divertor of the ITER concept during cleaning without costly additional heating systems; in addition, high temperature oxidation might cause failures on other components of the vessel. Experiments on thermal oxidation of codeposited layers with oxygen revealed, that codeposited layers from TFTR can be widely removed at this temperatures in a reasonable time span, whereas layers from ASDEX and TEXTOR and such produced in a laboratory require temperatures > 400 °C = 673 K for complete removal; a discussion of rates of fusion relevant a-C:D-specimen in oxygen is found in [1]. In this paper we examine ozone, being a more reactive oxygen modification consisting of 3 oxygen atoms, for its applicability in removal of thick a-C:D-layers from TEXTOR.

In addition, use of carbon materials as plasma facing components (PFC) in fusion reactors requires some safety concern due to the limited oxidation resistance of carbon at high temperatures: In accidents with ingress of oxidising media into the vacuum vessel [2] besides the

beforementioned release of radiotoxic materials bound onto the carbon also formation of burnable gases (CO or CO+H₂) and their explosion have to be taken into account in safety analyses. Accordingly, chemical kinetics of the oxidation reactions of C-based plasma facing materials has to be known. This paper gives a short overview of our oxidation measurements on fusion relevant C-based materials in steam and oxygen and outlines open problems.

2. Oxidation of codeposited layers in ozone

2.1 Background

Following fluorine, ozone (O₃) is the strongest oxidising agent. A RF-produced mixture of O₃ and atomic oxygen was already proposed by Post [3] for use as cleaning agent in fusion reactors. There are several methods of ozone formation available [4], silent electric discharge being predominately used for industrial applications. Thermal stability of ozone against decomposition to oxygen (O₂) is limited: Whereas its lifetime at room temperature is in the range of 3 days in absence of catalysts, it reduces at 250 °C (523 K) to roughly ≤ 0.1 s. Accordingly, ozone can be used as oxidiser at moderate temperatures (< 200 °C = 473 K), which however is not a disadvantage for use in fusion reactors, because of the beforementioned problems achieving temperatures higher than 250 °C (523 K) in ITER during cleaning.

Only a few publications on oxidation of carbon by ozone are available: In [5] Hennig found, that ozonisation of air leads to formation of several other oxidising agents, influencing the oxidation of carbon: Air flows through an ozoniser (silent electric discharge) and the 2 % of ozone containing exit gas passes over carbon; measured oxidation rates versus temperature reveal a maximum at 125 °C (398 K) with a value of 1 %/h; to lower temperatures the reactivity slows down with an activation energy of about 30 kJ/mol, and to higher temperatures a very steep rate decrease is observed. In contrast to that, ozone produced from oxygen (4 % O₃ in O₂) shows a normal Arrhenius like oxidation behaviour against graphite up to about 170 °C (443 K) with an activation energy of about 68 kJ/mol; however the oxidation rate of graphite in ozone from oxygen remains up to 130 °C (403 K) substantially (e.g. an order of magnitude at 100 °C (373 K)) smaller than in ozonised air, despite to the lower ozone concentration in the latter. This behaviour is explained by N₂O₅, always present in ozonised air, which dominates the carbon oxidation process by formation of lamellar compounds with the graphite lattice. N₂O₅ starts to decompose at about 100 °C (373 K), which is thought to be responsible for the decrease of rates with increasing temperature. Besides N₂O₅, an unidentified oxidising species is detected in ozonised air at temperatures > 120 °C (373 K). Comparing the reactivity of ozone with that of oxygen (air) against graphite it has to be noted, that oxidation in air requires temperatures of about 640 °C = 913 K for reaching a rate of 1 %/h [8,9], which is about 500 K higher than in ozonised oxygen or air.

In [6] graphite is oxidised in 6 % ozone produced from oxygen; in good agreement with the work of Hennig, an activation energy of 70 kJ/mol is measured at temperatures between 30 and 180 °C (303 - 453 K). Also, oxidation rates at 120 °C (393 K) are in the same range as those given in the study of Hennig. Preliminary measurements in our laboratory at 120 °C (393 K) and 3 % ozone from oxygen on a high purity nuclear graphite again resulted in an oxidation rate of about 1 %/h; however, oxidation of a hard a-C:D-layer (diamond like, laboratory produced by DIARC company, Finland) did not result in a measurable oxidation under similar conditions in a short term (2 h) experiment [7]. The oxidation behaviour of hard a-C:D-layers from fusion experiments has not yet been tested in ozone.

In this paper we will examine the oxidation behaviour of a-C:D-flakes from TEXTOR in ozone. These thick flakes have already been oxidised in oxygen of 21 kPa [1], but with the result, that a sufficient, continuous high oxidation rate cannot be obtained at temperatures $\leq 450\text{ }^{\circ}\text{C} = 723\text{ K}$, which are difficult to obtain in ITER. The present study will include oxidation of the ITER relevant carbon based first wall material NS31 in order to prove its damage in case of use of ozone in the vacuum vessel, together with a nuclear graphite; another reason for use of these materials is, that only a limited amount of TEXTOR flakes is available for these experiments and some general problems of oxidation with ozone can be studied with such carbon materials. Furtheron the question will be studied, whether there are similar differences in reactivity between ozonised oxygen and air as reported by Hennig; this is of interest, because of the higher oxidation rates in ozonised air at low temperatures.

2.2 Experiments and discussion

The facility for oxidation experiments with ozone consists of a supply of dry gas (synthetic air or oxygen), a commercial ozoniser based on silent electric discharges (produced by Sander, FRG), a furnace with a quartz container holding the specimen and a charcoal trap for decomposition of the surplus ozone. The ozoniser is calibrated by absorbing ozone in a buffered KI-solution and titration of formed iodine with $\text{Na}_2\text{S}_2\text{O}_3$. Weight loss of specimen is measured in certain time intervals. Gas flow used in experiments is 10-100 lSTP/h.

First experiments are performed in ozone produced from synthetic dry air with an ozone concentration of 0.4 % on A3-powder (high purity fine grain nuclear graphite containing about 10 % of ungraphitised binder) with a particle size of about 0.5 - 1 mm. Temperatures applied are between $120\text{ }^{\circ}\text{C}$ (393 K) and $170\text{ }^{\circ}\text{C}$ (443 K); following experience of Hennig, the oxidation rate should decrease here with temperature. Time of oxidation is between 1 and 5 h/run. For comparison, ozone produced from oxygen (0.8 %) is used in the same temperature range for additional measurements on A3. In these experiments in ozonised air we did not observe the beforementioned rate decrease with temperature, but a similar oxidation behaviour as in ozonised oxygen (a moderate rate increase with temperature). Due to the higher ozone concentration, the reaction in ozonised oxygen is slightly faster than in ozonised air (but the reaction order is below 1). Absolute weight loss rates we found are 1 - 3 %/h in ozonised air and 1.5 - 4 %/h in ozonised oxygen. We observed a smaller temperature dependence than measured in [5,6], which however might be due to the pronounced dependence of rate of A3 on burn-off (rate decreases at burn-off $> 5\%$): This is caused by the binder content of A3, which probably dominates the oxidation behaviour at low burn-off; this binder is known to be preferentially oxidised in O_2 and has also a lower activation energy in oxygen than the filler graphite [8]. Altogether, these measurements do not show an advantageous oxidation behaviour of ozonised air in comparison with ozonised oxygen and, because higher ozone concentrations are obtainable in ozonised oxygen, this oxidant is used in all following experiments.

Furtheron, we concentrated our experiments on thick TEXTOR-flakes (collected 1997 from graphite tiles of the toroidal belt limiter. Thickness: $20 \pm 5\text{ }\mu\text{m}$, D/C-ratio: about 0.04; impurities: about 15 weight-% of B and transition metals; about 5 mg of flakes are used in each experiment) on one temperature ($185\text{ }^{\circ}\text{C} = 458\text{ K}$), which is easily obtained in ITER and allows for a still sufficient life time of ozone. Results on these flakes are shown in fig. 1, which contains time dependent weight-loss and weight-loss rate for runs with flows of 10 and 100 lSTP/h (3.4 resp. 0.8 vol-% of ozone). Assuming a flake thickness of $20\text{ }\mu\text{m}$ and oxidation on all surfaces, a weight-loss rate of 10 %/h corresponds to an a-C:D-layer reduction rate of $1.25\text{ }\mu\text{m/h}$,

if the ash content is considered. It is obvious, that the rate starts at a high level (0.9 - 2.0 $\mu\text{m}/\text{h}$), but rapidly slows down to about 0.20 - 0.25 $\mu\text{m}/\text{h}$ until C is completely gasified, which is the case after about 24 h; it has to be noted, that during oxidation in oxygen the rate drops for TEXTOR-flakes to zero at temperatures $\leq 450\text{ }^\circ\text{C} = 723\text{ K}$ before complete carbon gasification [1], which underlines the favourable oxidation features of ozone. The lower layer reduction rate for low flow (despite the higher ozone concentration) is probably due to partial thermal ozone decomposition in that experiment, which overcompensates the increase of the layer reduction rate by the higher ozone level. The final weight-loss of about 75 % is consistent with the impurity content (forming solid oxides under substantial weight gain) and is observed in oxidation experiments in O_2 , too [1]. During oxidation the colour of the flakes changes from black to yellowish-golden, probably due to remaining metal/boron oxides.

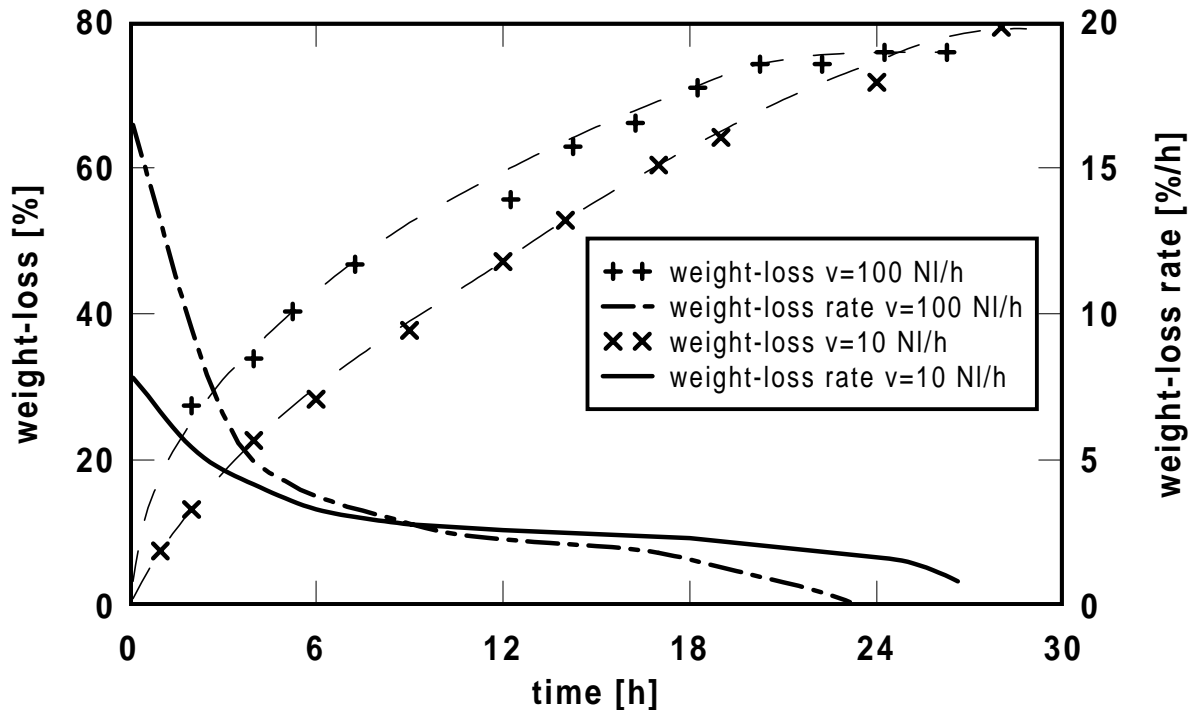


FIG. 1: Measured weight-loss and weight-loss rate of thick a-C:D TEXTOR-flakes in ozone at $185\text{ }^\circ\text{C} = 458\text{ K}$ for 2 different volume flows (v in $\text{NI}/\text{h} = l_{\text{STP}}/\text{h}$)

Comparison of these values with rates in O_2 is not easy, because in O_2 only partial C/D-gasification is possible at $\leq 450\text{ }^\circ\text{C} = 723\text{ K}$ [1]. Comparing maximum (starting) rates it becomes clear, that those in O_3 are similar to rates in O_2 ($0.3\text{ }\mu\text{m}/\text{h}$ for 673 K at 21 kPa O_2) at $> 200\text{ K}$ higher temperatures. This means, that ozone has some potential for use as cleaning oxidant; however, several questions remain open: Rate dependence on temperature and O_3 partial pressure has to be examined, the applicability for other kinds of a-C:H-layers has to be tested, and the optimum temperature considering both, increase of layer reduction rate and of O_3 decomposition with temperature has to be found out. Studies on oxidation resistance of other components of the vacuum vessel against O_3 might be necessary, too. We plan to use a suitably fitted thermogravimetric apparatus for future studies on oxidation of a-C:D-flakes in O_3 .

Oxidation of NS31 (3D CFC with 8-10 % of Si, reference material for ITER; specimen size: $10*5*1\text{ mm}$) in ozonised oxygen (3.4 % O_3 , flow: $10\text{ }l_{\text{STP}}/\text{h}$) at $185\text{ }^\circ\text{C} = 458\text{ K}$ for altogether 6 h resulted in an average weight-loss rate of $0.65\text{ } \%/ \text{h}$, which is much smaller than that of A3

and gives an indication of PFC damage during ozone application. It has to be noted, that the oxidation mechanism of porous carbons with ozone (regime I or II, i.e. the relevance of in-pore diffusion [9]) is not yet clear.

3. Survey on oxidation of plasma facing materials

An overview on our oxidation measurements in air/oxygen and steam is presented in [9]. We oxidised graphites, 2D and 3D CFCs (carbon fiber composites) and graphites/CFCs mixed with Si respectively Ti. In general we found, that doping of Si into the material increases the oxidation resistance, but reduction of oxidation rates by a factor of ≥ 100 requires large fractions of Si (40 vol-% SiC); for Si-contents $< 10\%$ the oxidation resistance is improved only by a factor of 2 - 4. Ti doping does not improve the oxidation stability, probably, because TiO_2 does not form a gas diffusion barrier as SiO_2 does. In CFCs, the primary attack goes onto the matrix, whereas the fibers are more stable [8]; there is a change in oxidation mechanism at intermediate temperatures, when the CFC-matrix is completely gasified (regime II with in-pore diffusion influence \rightarrow regime I with chemical control). Oxidation by steam requires roughly 300 K higher temperatures for reaching similar rates as in oxygen/air (oxidation regime II); however, comparing rates of different materials, the sequence in air is not always the same as in steam. Open questions include in-pore diffusion parameters of innovative carbon materials, an oxidation model for composite materials (including mixed materials) and detailed oxidation kinetics of C/Si mixed materials. We plan to perform extended studies on oxidation of Si-doped fusion relevant CFC-materials also connected to R&D for High Temperature Reactors (HTRs), where such advanced materials are needed, too.

4. References

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